Exploring $KTiPO_4F$ as an anode material for potassium-ion batteries

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Table S1. EDX elemental composition of the pristine powder sample

Spectrum number	K, at.%	Ti, at.%	P, at.%
1	31.17	34.42	34.41
2	29.50	35.25	35.25
3	30.67	34.67	34.66
4	29.5	35.25	35.25
5	30.63	34.69	34.68
6	29.29	35.35	35.36
7	31.46	34.27	34.27
8	31.32	34.35	34.34
9	32.19	33.9	33.91
10	32.09	33.95	33.96
11	32.03	33.99	33.99
12	33.48	33.26	33.26
13	31.78	34.11	34.11
14	25.76	37.12	37.12
15	33.08	33.46	33.45
16	33.48	33.27	33.26
17	31.21	34.4	34.39
18	32.27	33.87	33.86
19	35.95	32.03	32.02
20	31.26	34.38	34.37
21	29.97	35.01	35.02
22	29.48	35.26	35.26
23	29.07	35.47	35.46
24	29.36	35.32	35.32
25	35.46	32.27	32.27
Avg.	**31.26**	**34.37**	**34.37**
Std. error	**0.4**	**0.2**	**0.2**

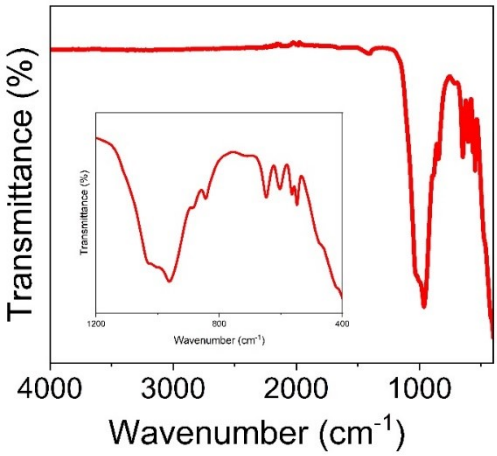

Fig. S1 FTIR spectrum of pristine KTPF powder in the range of 4000-400 cm^{-1} range (Inset: the enlarged spectrum in the range of 1200-400 cm^{-1}).

Table S2. The comparison of potassium atom position, fraction, and thermal displacement of the current study (the black colour) with the previous report (the red colour).[1]

Atoms	X, Å	Y, Å	Z, Å	Fraction	U_{iso}(Å^2)
K1	0.3762(7)	0.7786(1)	0.3057(9)	0.709(5)	0.019(7)
K1′	0.4122(7)	0.8524(13)	0.4428(7)	0.260(7)	0.014(4)
K2	0.1130(9)	0.6582(13)	0.0235(11)	0.176(6)	0.040(2)
K2_	0.0892(3)	0.6873(5)	0.1659(5)	0.300(7)	0.045(4)
K2'_	0.1093(2)	0.7230(3)	0.0733(5)	0.576(7)	0.017(3)
K1	0.3789(5)	0.7798(9)	0.3045(8)	0.732(7)	0.016(2)
K1′	0.3999(17)	0.830(3)	0.4330(19)	0.268(7)	0.016(2)
K2	0.086(2)	0.632(5)	-0.012(3)	0.151(10)	0.033(3)
K2_	0.0875(13)	0.703(3)	0.158(2)	0.264(13)	0.033(3)
K2'_	0.01051(8)	0.7258(17)	0.0678(12)	0.585(17)	0.033(3)

Table S3. Atomic positions, occupancies, and ADPs for $KTiPO_4F$

Atoms		x, Å	y, Å	z, Å	Fraction	U_{iso}, Å^2
K1	K	0.3762(7)	0.7786(1)	0.3057(9)	0.709(5)	0.019(7)
K1'	K	0.4122(7)	0.8524(13)	0.4428(7)	0.260(7)	0.014(4)
K2	K	0.1130(9)	0.6582(13)	0.0235(11)	0.176(6)	0.040(2)
K2_	K	0.0892(3)	0.6873(5)	0.1659(5)	0.300(7)	0.045(4)
K2'_	K	0.1093(2)	0.7230(3)	0.0733(5)	0.576(7)	0.017(3)
Ti1	Ti	0.3867(2)	0.4951(9)	0.0022(7)	1	0.0255(6)
Ti2	Ti	0.2448(4)	0.2574(10)	0.2564(9)	1	0.0255(6)
P1	P	0.5002(7)	0.3292(5)	0.2573(11)	1	0.0157(8)
P2	P	0.1798(3)	0.5039(15)	0.5054(13)	1	0.0157(8)
O1	O	0.4758(7)	0.4903(18)	0.1545(11)	1	0.0080(12)
O2	O	0.4981(12)	0.4567(17)	0.3803(11)	1	0.0080(12)
O3	O	0.4045(8)	0.2017(18)	0.2804(16)	1	0.0080(12)
O4	O	0.5953(8)	0.1893(18)	0.2386(14)	1	0.0080(12)
O5	O	0.1220(10)	0.3082(16)	0.5454(13)	1	0.0080(12)
O6	O	0.1066(10)	0.6862(16)	0.4842(14)	1	0.0080(12)
O7	O	0.2574(10)	0.540(3)	0.6112(13)	1	0.0080(12)
O8	O	0.2459(11)	0.463(3)	0.3889(12)	1	0.0080(12)
F1	F	0.2706(12)	0.534(3)	0.8845(13)	1	0.0208(19)
F2	F	0.2752(11)	0.494(3)	0.1308(12)	1	0.0208(19)

Table S4. Selected interatomic distances for $KTiPO_4F$

Bond	Distance, Å	Bond	Distance, Å
Ti1-O1	2.008(2)	Ti2-O3	2.123(1)
Ti1-O2	2.015(2)	Ti2-O4	1.983(3)
Ti1-O5	2.070(1)	Ti2-O7	2.097(2)
Ti1-O6	1.998(3)	Ti2-O8	1.945(9)
Ti1-F1	1.987(7)	Ti2-F1	2.001(8)
Ti1-F2	2.005(6)	Ti2-F2	2.073(10)
P1-O1	1.549(7)	P2-O5	1.528(8)
P1-O2	1.558(6)	P2-O6	1.527(2)
P1-O3	1.511(9)	P2-O7	1.539(2)
P1-O4	1.542(4)	P2-O8	1.543(9)

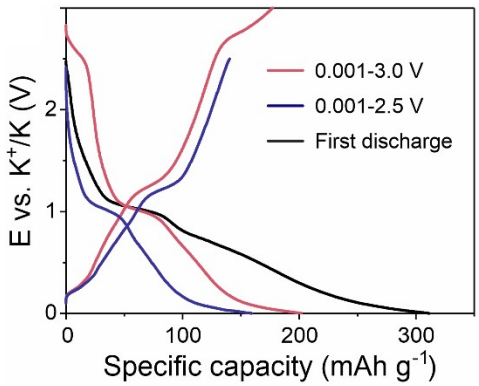

Fig. S2 Galvanostatic charge and discharge profiles in the potential range of 0.001-3.0 V and 0.001-2.5 V including the first discharge.

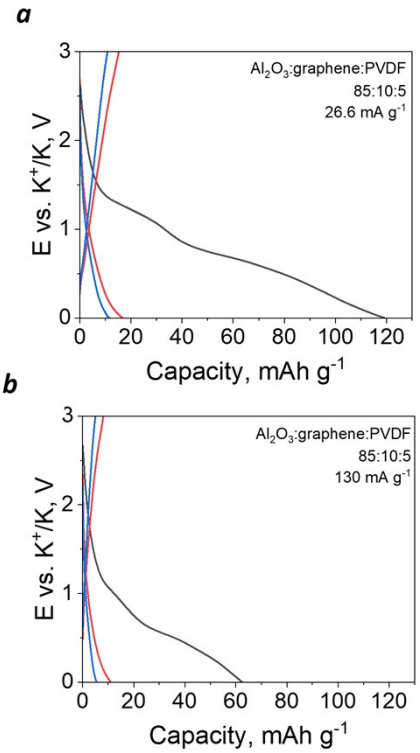

Fig. S3 The contribution of graphene nanoplate (GN) to the capacity at a) the current density 26.6 mA g^{-1}(C/5 rate) and b) current density 130 mA g^{-1} (C rate).

Table S5. O:F ratio in pristine $KTiPO_4F$ powder sample calculated from EDX analysis.

Spectrum number	O, at.%	F, at.%
1	80.5	19.5
2	80.7	19.4
3	80.9	19.1
4	80.5	19.5
5	80.9	19.1
6	80.2	19.8
7	80.6	19.4
8	80.9	19.1
9	80.0	20.0
10	80.4	19.6
11	80.3	19.7
12	80.7	19.3
13	80.8	19.3
14	80.8	19.2
15	79.6	20.4
16	80.0	20.0
17	80.6	19.5
18	80.6	19.4
19	79.8	20.2
20	79.9	20.1
Avg.	**80.4**	**19.6**
Std. dev.	**0.4**	**0.4**

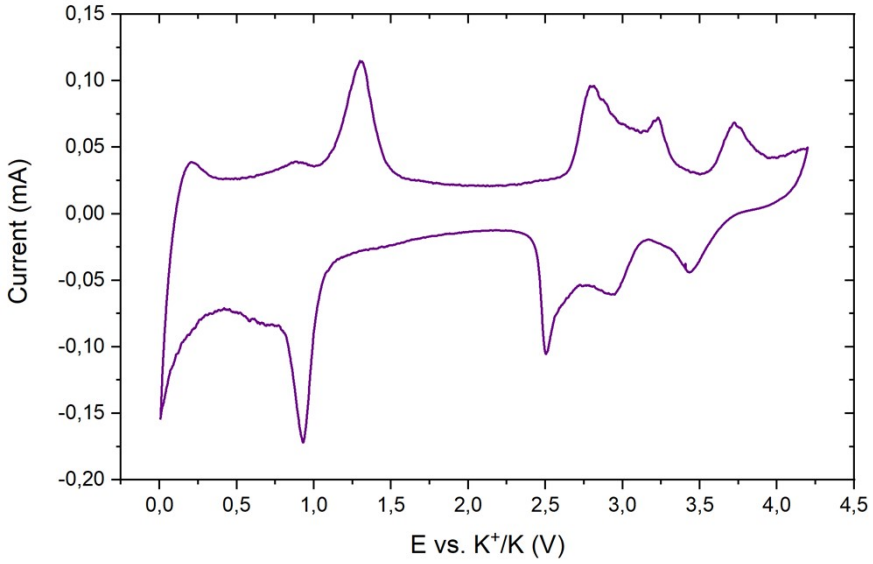

Fig. S4 Cyclic voltammogram of KTPF in the 0.001 – 4.2 V potential range at 100 µV s^{-1} scan rate.

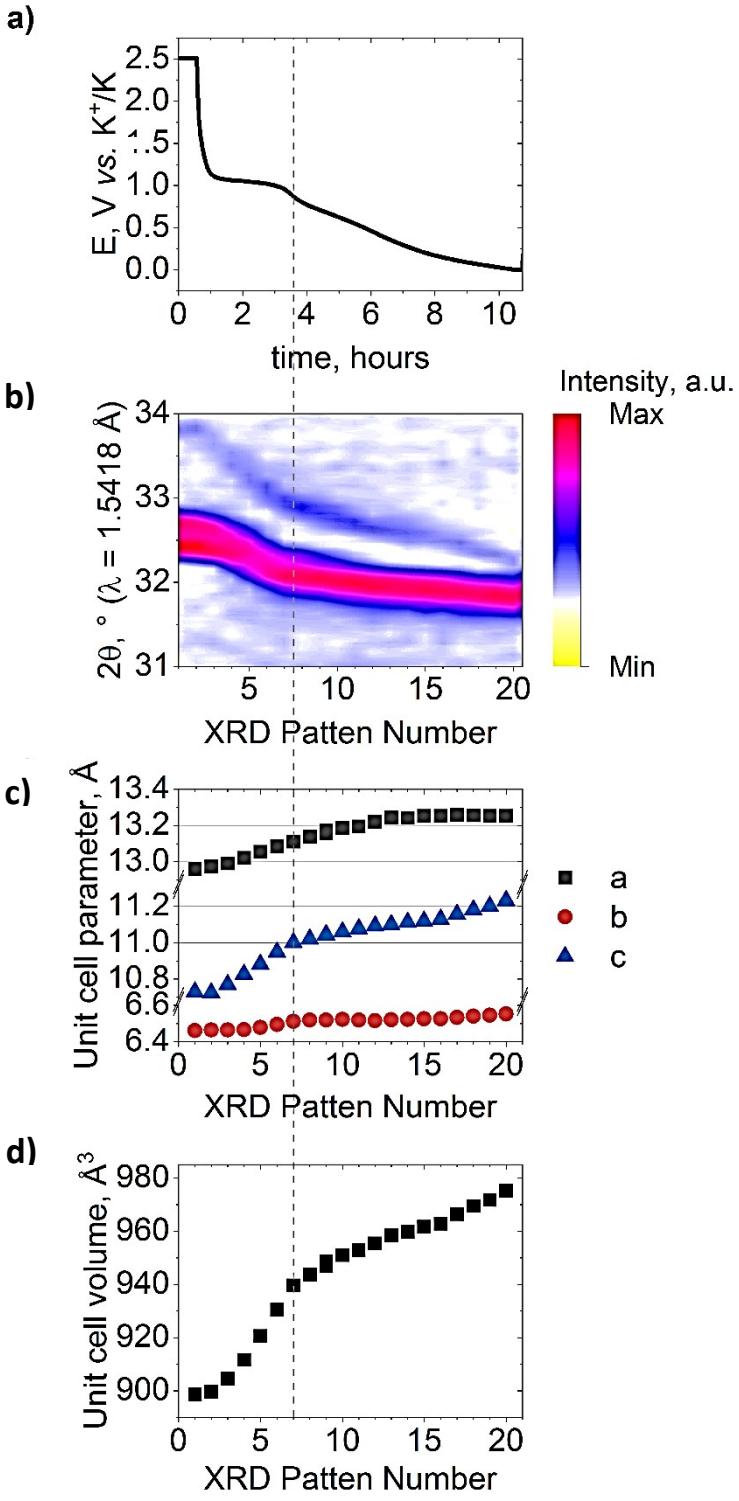

Fig. S5 Phase and cell parameters alteration study of KTPF. a) the first discharge (from OCV) of KTPF||K cell during *operando* XRD study b) *operando* XRD patterns at the angle of 31-33 (degrees), 411 and 221 reflections c) *a*, *b* and *c* parameter change upon intercalation of K-ion d) Unit cell volume change trend during operando XRD measurement.

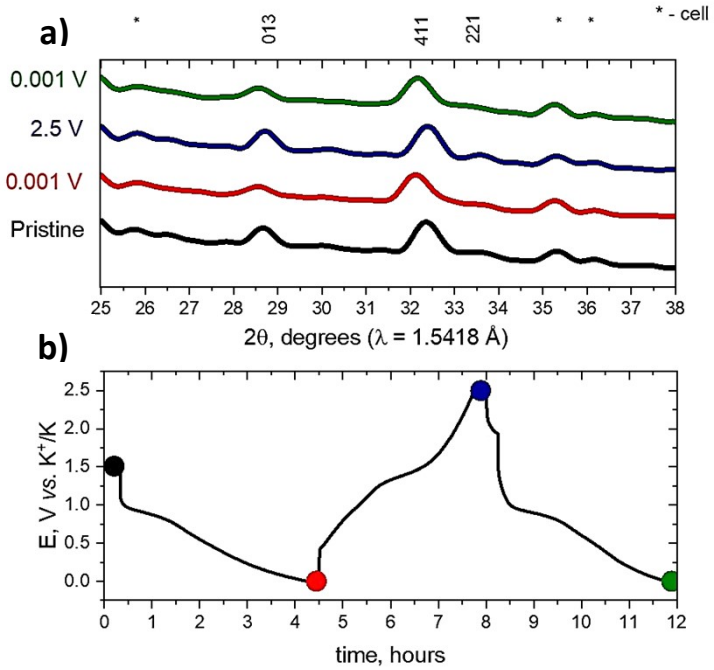

Fig. S6 The reversibility study of KTPF//K cell with operando XRD a) the recorded operando XRD patterns b) discharge and charge of the pre-cycled half-cell from OCV. The star sign (*) marks the reflections from the cell components (which remain unchanged during the operando experiment).

Table S6. The comprehensive comparison of KTPF with the reported polyanion benchmarks.

Active material (Structure)	Theoretical capacity (mAh g^{-1})	Electrode composition (weight ratio) AM = active material	Electrolyte formulation	Reversible capacity (mAh g^{-1}) @current (mA g^{-1})	Potential window (V)	Capacity retention (%), cycles @ current density (mA g^{-1})	ICE (%)	Ref
This work (Orthorhombic)	133	AM:G: PVdF=8.5:1:0.5	1 M KPF_6 in EC:PC (1:1 v/v)	205 @ 26.6	0.001-3	99, 1000 @ 130	57	
$KVPO_4F$ (Orthorhombic)	131.4	AM:SP: PVdF=7:2:1	1 M KPF_6 in EC:PC (1:1 v/v)	105 @ 100	0-3	91, 100 @ 100	51	[2]
$K_{0.76}V_{0.55}Nb_{0.45}OPO_4$ (Orthorhombic)	97	AM:SP: CMC=8:1:1	5 M KFSI in DEGDME	82.6 @ 3	0.1-1.8	66.4, 550 @ 5	53	[3]
$K_{2.13}V_{1.52}Ti_{0.48}(PO_4)_3$ (Orthorhombic)	137	AM:SP: CMC=8:1:1	5 M KFSI in DEGDME	136 @ 10	0.01-2.5	69.3, 1000 @ 100	49.63	[4]
$KTiOPO_4$-rGO (Orthorhombic)	135	AM:AB: SA =8:1:1	1 mol dm^{-3} KFSA in EC: DEC (1:1 v/v)	125 @ 10	0.1-2.5	84, 70 @ 20	67	[5]
$KTiOPO_4$ (Orthorhombic)	150	N/A	N/A	176.7 @ 30	0-3	78.4, 10000 @ 3000	51.5	[6]
$K_2Ti_8O_{17}$ (Monoclinic)	308	AM:SP: PVDF=7:2:1	0.8 M KPF_6 EC:DEC (1:1 v/v)	109 @20	0.01-3	62.7, 50 @ 20	57	[7]
$K_2Ti_4O_9$ (Monoclinic)	129	AM:AB: PVDF=7:2:1	1 M KPF_6 in EC:PC (1:1 v/v)	90 @30	0-2.5	47.3, 30 @ 100	18	[8]
$K_2Ti_4O_9$ (Monoclinic)	129	AM: PVDF=7:2:1	1M KPF_6 in Diglyme	122 @ 20	0.01-3	61, 100 @ 50	23%	[9]
H-TiO_2-C MTs (Hetero-structure)	N/A	N/A	0.8 M KPF_6 In EC:DEC (1:1 v/v)	197.5 @ 200	0.01-3.0.	81.3, 1200 @ 500	49.1	[10]
$KTi_2(PO_4)_3$@C or (KTPO@C) (Rhombohedral)	N/A	AM:SP:CMC=7:2:1	0.8 M KPF_6 in EC/DEC (1:1 v/v)	250 @ 20	0.01-3.	34, 1000 @ 1000	64.5	[11]
π-$Ti_2O(PO_4)_2$	N/A	AM: SP:CMC=8:1:1	3 M KFSI in 1,2-DME	224 @ 100	0.01-3	82.5, 2000 @ 1000	55.5	[12]
$CrPO_4$@NC (Orthorhombic)	N/A	AM: AB: PVDF= 7:2:1	1 M KFSI in EC: DEC (1:1 v/v)	300 @ 50	0.01-3.0	74.3, 100 @ 200	43.1	[13]
VPO_4 (Amorphous)	550	AM:AB: CMC=7:2:1	3 M KFSI in DME	390 @ 50	0.01-3.0	90, 500 @ 500	63.8	[14]
TiP_2O_7 (Cubic)	N/A	AM:SP: PVDF=8:1:1	0.8 M KPF_6 in EC:DEC (1:1 v/v)	321 @ 100	0.01-3	56, 5000 @ 1000	45	[15]
$Co_2P_2O_7$/C (N/A)	N/A	AM:SP: CMC=7:2:1	1 M KFSI in DME	441 @ 100	0.01-3	62, 900 @ 1000	N/A	[16]
CoC_2O_4/CNTs (Monoclinic)	400	AM:SP: PAA=8:1:1	0.5 M KPF_6 in PC:FEC (98:2 v/v)	400 @ 100	0-3	73, 200 @ 40	51.5	[17]
$Co(PO_3)_2$NSs/CC (Monoclinic)	N/A	100% of AM	0.8 M KPF_6 in EC:DEC (1:1 v/v)	700 @ 50	0-1.5	83, 50 @ 500	57	[18]

Table S7: The comparison of half-cell specification of graphite, hard carbon, and KTPF.

Anode materials	Average potential, V	Theoretical Capacity, mAh g^{-1}	Rate performance @ current rate	Long-cycling performance; (capacity, mAh g^{-1})	Ref.
KTPF	0.8	133.4	50 mAh g^{-1} @ 7.5 C	1000 cycles @ 1C; (130)	This work
Commercial graphite	0.1	279	50 mAh g^{-1} @ 0.7 C	200 cycles @ 0.036 C; (80)	[19]
Expanded graphite	0.1	279	176 mAh g^{-1} @ 0.7 C	500 cycles @ 0.7 C; (176)	[19]
Hard Carbon	0.3	279	44.4 mAh g^{-1} @ 10 C	400 cycles @ 0.2 C (200)	[20]

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